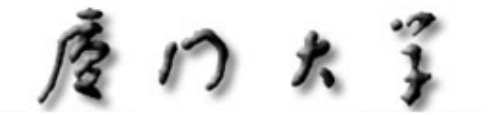
学校编码：10384　　分类号＿＿＿密级＿＿＿
学号：200425022　　UDC＿＿＿＿＿＿＿



硕　士　学　位　论　文

分子识别型高分子智能水凝胶的合成、表征及分析应用初探

Synthesis and Characterization of Intelligent Polymer Hydrogels and Preliminary Study on Their Applications in Analytical Chemistry

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论文提交日期：2007 年 6 月
论文答辩时间：2007 年 7 月
学位授予日期：2007 年　月

答辩委员会主席：＿＿＿＿＿＿
评　　阅　　人：＿＿＿＿＿＿
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2007 年 6 月

Synthesis and Characterization of Intelligent Polymer Hydrogels and Preliminary Study on Their Applications in Analytical Chemistry

A Thesis Submitted to

the Graduates School of Xiamen University for the Degree of

Master of Science

by

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June 2007

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摘 要

本文将聚N-异丙基丙烯酰胺（PNIPAM）的智能性与β-环糊精（β-CD）对客体分子的识别和包络特性相结合，合成了三种具有分子识别能力的多功能β-环糊精智能水凝胶，并对这三种凝胶材料的智能特性和对客体分子的包络能力以及分析应用前景进行了初步研究。全文共分为四章。

第一章综述了智能高分子凝胶、高分子环糊精和多环芳烃检测的研究进展。首先，以体积相变原理为基础，从溶剂、温度、pH值、光辐射、电场、磁场等方面阐述了智能高分子凝胶对环境的敏感性，同时介绍了智能高分子凝胶在生物医学工程、药物控制释放、免疫分析、生物分离分析等方面的应用。其次，介绍了环糊精、环糊精衍生物及环糊精高分子在分析化学中的应用研究。再其次，对多环芳烃的性质、结构进行了简述，综述了多环芳烃的分析测定方法。在文献综述的基础上，提出了本论文的研究目的和研究设想。

第二章开展了N-异丙基丙烯酰胺-N-烯丙胺代-β-环糊精共聚水凝胶（ACD/PNIPAM）的合成和表征研究，并探讨了ACD/PNIPAM水凝胶与芘的相互作用及其在环境修复中的应用前景。首先通过磺酰化修饰，制得6位单修饰的磺酰化β-CD (6-OTs-β-CD)，然后将6-OTs-β-CD与烯丙胺反应，得到烯丙胺修饰的β-CD单体N-烯丙胺代-β-环糊精（ACD)。最后通过自由基聚合法将ACD与N-异丙基丙烯酰胺（(NIPAM）共聚，制得β-CD修饰的智能型水凝胶ACD/PNIPAM。通过核磁共振（NMR）、红外光谱（IR）、质谱（MS）等分析测试手段对水凝胶ACD/PNIPAM进行了表征，利用电子显微镜技术对ACD/PNIPAM共聚物的型貌进行了分析，利用荧光光谱技术研究了ACD/PNIPAM水凝胶对芘的分子识别特性，探讨了其在环境分析中的应用前景。

第三章开展了N-异丙基丙烯酰胺-丁基二酸单酯化-β-CD共聚水凝胶（MAH-β-CD/PNIPAM）的合成和表征研究，并探讨了MAH-β-CD/PNIPAM水凝胶与多环芳烃客体分子的包络作用及其在分析化学中的应用前景。首先用顺丁烯二酸酐（MAH）对β-CD进行化学改性，合成出了丁烯二酸单酯化β-CD单体（MAH-β-CD），然后通过氧化还原自由基引发MAH-β-CD与NIPAM聚合，合成了MAH-β-CD/PNIPAM共聚水凝胶。用核磁共振（NMR）、红外光谱（IR）及质谱（MS）对MAH-β-CD单体及共聚物进行了表征；用电镜技术观测MAH-β-CD/

PNIPAM共聚物的形貌；考察了MAH-β-CD/ PNIPAM 水凝胶的智能特性，同时利用荧光显微技术和荧光光谱研究了MAH-β-CD/ PNIAM水凝胶的分子识别特性、分离特性以及分辨和分别测定特性，揭示了MAH-β-CD/ PNIAM水凝胶的应用前景。

第四章开展了N-异丙基丙烯酰胺-co-丙烯酸-乙醇胺代-β-CD离子聚合物水凝胶（EAA-β-CD/AA/PNIPAM）的合成和表征，并探讨了EAA-β-CD/AA/PNIPAM水凝胶与多环芳烃客体分子的包络作用以及在分析化学中的应用前景。首先通过NIPAM与少量AA共聚，得到AA/PNIPAM，使PNIPAM主链带上可负离子化的羧基(-COOH)；其次用乙醇胺（EAA）与磺酰化修饰的6-OTs-β-CD反应，生成N-乙醇胺代β-CD（EAA-β-CD），使β-CD带上可正离子化的仲胺基(-NH-)；最后二者通过$-COO^-$和$-NH_2^+$-的离子缔合相互作用形成EAA-β-CD/AA/PNIPAM离子聚合物。用核磁共振（NMR）、红外光谱（IR）及质谱（MS）对其单体及离子聚合物进行了表征，用扫描电镜观测了EAA-β-CD/AA/PNIPAM离子聚合物的形貌。考察了水凝胶的智能特性，同时利用荧光显微技术和荧光光谱研究了EAA-β-CD/AA/PNIPAM 离子聚合物水凝胶的分子识别特性、分离特性以及分辨和分别测定特性，揭示了EAA-β-CD/AA/PNIPAM 离子聚合物的应用前景。

关键词 β-环糊精；N-异丙基丙烯酰胺；智能水凝胶；分子识别；应用前景

ABSTRACT

Three kinds of the dual-funational N-isoprylacrylamide-co-β-Cyclodextrin Smart Hydrogels, which contain an environmental sensitivity component and a molecular inclusion function component, were systhesized. Based on their special functionalities, the smart property and the molecular inclusion ability of these hydrogels were studied, and their application prospects in analytical chemistry were discussed. This thesis consists of four chapters.

In chapter one, the literature on the research and application of the intelligent polymer hydrogels, β-Cyclodextrin polymer derivatives and PAHs was summarized. The chapter first described the intelligent polymer gels to the environment sensitivity in several areas such as the solvent, temperature, pH, light radiation, the electric field, magnetic fields and so on, based on the Volume Phase Transition theory and introduced the applications of the smart polymer gels in biomedical engineering, controlling drug release, immunoassay and bioseparation analysis. Then, it described the research and applications of cyclodextrins (CDs), cyclodextrin derivatives and cyclodextrin polymer in analytical chemistry. Thirdly, the chapter summaried the properties and structures of the PAHs and overviewed the analysis of PAHs. Finally, the research objectives and considerations were proposed.

In chapter two, the polymer N-isopropylacrylamide-N-allylamino-β-cyclodextrin hydrogel (ACD/PNIPAM) was synthesized and characterized. The research and applications of the interaction between the ACD/PNIPAM with pyrene in the environment analysis were discused. First of all, mono-6-deoxy-6-(p-tolylsulfonyl)-cyclodextrin (6-OTs-β-CD) was prepared. Then the β-CD monomer, N-allylamino-modified-β-cyclodextrin (ACD), was synthesized via the reaction of 6-OTs-β-CD with allylamino. Finally, ACD/NIPAM, β-cyclodextrin smart hydrogel was synthesized through the free radical polymerization of ACD monomer with NIPAM monomer. The ACD monomer and the ACD/NIPAM copolymer hydrogel were characterized by Nuclear Magnetic Resonance (NMR), Infrared spectroscopy (IR), Mass spectrometry (MS), and so on. The interior

morphology of ACD/PNIPAM copolymer hydrogel was observed by Scaning Electronic Microscopy (SEM). The characteristics of the Smart Hydrogel ACD/PNIAM on molecular recognition, separation properties and determination properties were studied by using Fluorescence Microscopy and Fluorescence spectrocopy. Interaction between the ACD/PNIPAM hydrogel with the PAHs molecules was investigated. The ACD/PNIPAM hydrogel showed a good application prospect in environmental analysis.

In chapter three, the MAH-β-CD/PNIPAM copolymer hydrogel was synthesized and characterized. The temperature sensitivity and the molecular inclusion ability of the MAH-β-CD/PNIPAM hydrogel was discussed. First of all, a β-CD based monomer with vivyl carboxylic acid groups via reaction of β-CD with maleic anhydride (MAH) was prepared. Then MAH-β-CD/PNIPAM hydrogel was synthesized from the free radical-redox polymerization. The MAH-β-CD monomer and the copolymer hydrogel were characterized by Nuclear Magnetic Resonance (NMR), Infrared spectroscopy (IR) and Mass spectrometry (MS) and so on. The interior morphology of MAH-β-CD/PNIPAM copolymer hydrogel was investigated by Scaning Electronic Microscopy (SEM). By using Fluorescence Microscopy and Fluorescence spectroscopy, the characteristics of the Smart Hydrogel MAH-β-CD/PNIAM on molecular recognition, separation properties and determination properties were studied. Interaction between the MAH-β-CD/PNIPAM hydrogel with the PAHs molecules was investigated. The MAH-β-CD/PNIPAM hydrogel showed a good application prospect in analytical chemistry.

In chapter four, a poly(N-isopropylacrylamide-co-acrylic acid)-6-ethanolamine-β-cyclodextrin ionic polymer (EAA-β-CD/AA/PNIPAM) was synthesized and characterized, and the temperature sensitivity and the molecular inclusion ability of the EAA-β-CD/AA/PNIPAM ionic polymer hydrogel was discussed. First of all, the poly(N-isopropylacrylamide-co-acryl acid) (poly(NIPAM-co-AA)) was prepared from the polymerization of NIPAM with AA. Then, EAA-β-CD was prepared via the reaction of mono-6-OTs-β-CD with EAA. Finally, a EAA-β-CD/AA/PNIPAM smart hydrogel was synthesized by the reaction of poly(NIPAM-co-AA) with EAA-β-CD.

The EAA-β-CD monomer and the ionic polymer hydrogel were characterized by Nuclear Magnetic Resonance (NMR), Infrared spectroscopy (IR) and Mass spectrometry (MS) and so on. The interior morphology of EAA-β-CD/AA/PNIPAM ionic polymer hydrogel was observed by Scaning Electronic Microscopy (SEM). By using Fluorescence Microscopy and Fluorescence spectrocopy, the characteristics of the smart ionic hydrogel EAA-β-CD/AA/PNIPAM on molecular recognition, separation properties and determination properties were studied. Interaction between the EAA-β-CD/AA/PNIPAM ionic polymer hydrogel with the object PAHs molecules was investigated. EAA-β-CD/AA/PNIPAM ionic polymer hydrogel showed a good application prospect in analytical chemistry.

Keywords: β-cyclodextrin; N-isopropylacrylamide; Intelligent hydrogels; Molecular Recognition; Application.

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